#3

PATENT SPECIFICATION

(11) 1 455 148

1 455 148

(21) Application No. 58483/73 (22) Filed 18 Dec. 1973
(31) Convention Application No. 66730
(32) Filed 21 Dec. 1972 in
(33) Luxembourg (LU)
(44) Complete Specification published 10 Nov. 1976
(51) INT CL² C01B 13/14
(52) Index at acceptance
C1A 13 N10B N11 N13A N21 N22 N24A N28 N30 N31 N33 N37 N38 N39A1 N40 N42 N48A N4A1A N56 N5A N7 N8 N9 NX1A
C1N 212 213 251 261 269 275 347 35Y 38X 402 414 432 436 440 447 473 477 478 480 481 490 492 515 517 526 590 591 592 59X 742 743 745 752 754 755 75Y 767 76Y

(19) THE PATENT OFFICE LONDON

(54) OXIDE COATING METHOD

(71) We, GLAVERBEL - MECANIVER, a Belgian Body Corporate of 166 Chaussee de La Hulpe, Watermael-Boitsfort, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of forming a metal oxide or silicon oxide coating on a substrate. The invention also relates to substrates to which a coating has been applied by such method.

It is well known that metal oxide coatings, for example cobalt oxide coatings, can be made by spraying an aqueous solution of a hydrated metallic salt, for example an aqueous solution of $CoCl_2.6H_2O$ or $FeCl_3.6H_2O$, onto the surface of a substrate which is heated to a temperature high enough to result in conversion of the metallic salt *in situ*. When this method is carried out the coating is usually of poor quality, particularly as regards the degree of uniformity of the thickness and the composition of such a coating. For example, when such an aqueous cobalt salt solution is applied, the result is equivalent to a granular deposit of irregular thickness and, usually, the coating has very poor adherence to the substrate. Coatings formed in this way are readily removed in the form of dust, simply by passing a finger over the coating or by applying a piece of adhesive tape onto the coating and then peeling the tape away.

One of the aims of the invention is to provide a method whereby metallic oxide or silicon oxide coatings of uniform thickness and composition can be readily produced on various substrates. More particularly it is an object of the invention to provide a method whereby metallic oxide or silicon oxide coatings having a high degree of uniformity can be formed on the surface of at least partly vitreous substrates, so that the said method can be used for forming optical films on vitreous bodies or articles, for example glazing sheets, windscreens, patterned glass and lenses for sunglasses.

Another object of the invention is to provide a method whereby metallic oxide or silicon oxide coatings can be produced which have antistatic or electrically conductive properties.

According to the present invention there is provided a method of forming a coating on a substrate, the coating comprising an oxide or oxides of one or more metals and/or of silicon in which method a solution comprising at least one metal compound and/or a silicon compound is applied to the substrate and the said compound or compounds is/are converted *in situ* by the action of heat so as to form a said coating, the said solution which is applied to the substrate being a solution of one or more metallic salts and/or a silicon salt selected from the group of acetates, halides and nitrates in a naprotic solvent having a dielectric constant greater than 15 and a dipole moment greater than 3D (D = Debye unit).

This method is of particular importance for coating vitreous or partly vitreous substrates. It can however also be used with advantage for coating non-vitreous substrates.

By means of the method according to the invention it is possible to produce oxide coatings whose thickness and composition are substantially uniform, this being essential, for example, in the case of very thin high light-transmission coatings and in the case of coatings which are required to have a definite electrical resistance.

The method is therefore suitable for forming optical films on vitreous bodies or articles so as to modify their light transmission and/or their light reflection, for example, in order to give the said bodies or articles a tinted appearance when viewed by transmitted or reflected light. The method is also very important for forming anti-static or conductive films on sub-

no
E7270
200

AD on "at least 400 nm"

Q. Is this a low E panel or a solar control panel?

Get better coating from a particular solution.

strates of a non-conductive material.

The uniformity of the coating which is made possible by the invention is due not only to the metallic salt used but also to the nature of the solvent.

The salt solutions used in carrying out the invention may be obtained at very low cost and enable metallic oxide and silicon oxide coatings to be produced very profitably on an industrial scale. The said salt solutions can moreover be relatively concentrated and this is advantageous particularly when the solution is required to be applied to a substrate which is moving fairly rapidly with respect to a coating station. Another important factor is the safety with which such solvents can be used under very high temperature conditions. It is therefore possible to heat and evaporate the solvent very rapidly and obtain a rapid conversion of the metallic and/or silicon compound or compounds, and this is also an important factor in the formation of coatings of uniform density.

The method can be used for obtaining a wide range of properties pertaining to the applied coating, by appropriate selection of the applied salts. The applied solution may contain a single metal salt or a silicon salt or a mixture of two or more salts of different elements. There is thus a great flexibility in the method for producing coatings which have definite optical or electrical characteristics. For example, it is possible to produce coatings composed of cobalt, iron and chromic oxides, by using a solution comprising cobalt acetate, ferric chloride and chromium nitrate.

Preferably, the substrate is preheated to a temperature high enough to provide the heat required to produce the said conversion of the applied compound or compounds.

Preheating of the substrate results in evaporation of the solvent and conversion of the applied compound or compounds immediately, i.e. as soon as the solution comes into contact with the substrate.

As already indicated, rapid conversion promotes uniformity of the coating.

Generally, in order to achieve the purposes primarily in view, the optimum temperature of the substrate when the coating process is carried out is in the range 300 to 700°C. The temperature will generally preferably be selected so as to be as high as possible consistent with avoiding any risk of damage to the substrate. When coating vitreous substrates, it is recommended to work in the temperature range 450 to 650°C. With a temperature between these limits very uniform coatings are obtained together with very good adherence of the coating to vitreous substrates, such adherence also being influenced by the temperature of the substrate at the moment the coating solution is applied.

The salt solution is preferably applied in the form of droplets. The required results are obtained most readily by applying the solution in such a form. For example, an internal mix spray gun may be used, which is fed with compressed air and salt soltion separately, both at the same, above atmospheric, pressure. The salt solution itself may be at ambient temperature or at a higher temperature provided that there is no undesirable premature evaporation of the solvent and no decomposition and oxidation of the applied compound or compounds and provided that the substrate is not exposed to harmful thermal shock.

As already stated the results attainable by the method according to the invention are due in part to the selection of an aprotic solvent having a dielectric constant greater than 15 and a dipole moment greater than 3D. As examples of aprotic solvents having such properties, the following are cited: dimethylformamide, dimethylacetamide, tetramethyl urea, dimethylsulphoxide, acetonitrile, nitrobenzene, ethylene carbonate, tetramethylene sulphone, hexamethylphosphoramide.

Special preference is given to dimethylformamide. This solvent is particularly suitable for most of the salts in question, so that these compounds may be applied in relatively high concentrations, which means that the rate of application of the solution to a given zone of the surface of a substrate can be relatively low to produce a coating of a given thickness. Dimethylformamide can also be used to apply coatings to substrates at very high temperatures without the risk of fire or explosion.

Preference is given to embodiments of the invention wherein the solution which is applied to the substrate comprises one or more acetates, halides or nitrates of an element or elements selected from the following group: Mg, Zr, V, Cr, W, Mn, Fe, Co, Ni, Cu, Zn, Cd, In, Sn, Pb, Bi, Th, Si.

It is advantageous to use in admixture with one or more of the said salts, one or more acetates, halides or nitrates, of a metal or metals selected from the group; Au, Ti, Ce, Mo, Sb, Al, As, Rh.

It should be noted that the coating formed on the substrate is not necessarily formed exclusively by an oxide or oxides of one or more metals and/or silicon, but may also contain an element, for example gold, in the metallic state. Generally, all the above-mentioned salts may be used in admixture with the selected solvent or solvents without any special precautions except those well known to those versed in the art which are intended to obviate undesirable redox or hydrolysis reactions in the solution.

When such solutions are used, it is possible to form thin, very high-quality oxide coatings which modify the light reflection and transmission of the substrate, and oxides which adhere perfectly to ceramic substrates and to glass and partly vitreous e.g. vitrocrystalline or vitroceramic substrates, which are the

materials primarily requiring an optical coating. It is also possible to form thin oxide coatings of a controlled electrical resistance satisfying given specifications. In this latter case, the coatings are applied preferably to non-conductive substrates such as glasses, ceramics, and vitrocrystalline or vitroceramic materials.

Advantageously, acetylacetone is also present in the applied salt solution. The presence of acetylacetone is generally particularly advantageous when applying a solution of one or more halides or nitrates. The acetylacetone enables optimum solution filmability to be obtained and makes possible a better pyrolysis of the metallic compounds.

For example, it is possible to obtain coatings of improved optical quality by adding acetylacetone to solutions comprising vanadium chloride, chromium nitrate, iron or nickel nitrate, or indium nitrate.

In some cases, the presence of acetylacetone ensures better safety in the preparation of the film-forming solution. If, for example, it is required to prepare a solution of anhydrous $SnCl_4$ in dimethylformamide, it is preferable first to mix the stannic chloride with acetylacetone and to pour the resulting liquid into the selected solvent to prevent the latter from igniting.

It has been found that when acetylacetone is used it is preferable to use proportions such that the number of moles of acetylacetone used is n times the number of moles of salt used (where n represents the valency or the aggregate of the valencies of the cation(s)).

As already indicated, the invention has been found particularly important for forming oxide coatings on vitreous and partially vitreous substrates, such as substrates of vitrocrystalline or vitroceramic material. This is due to the fact that the method enables thin oxide coatings to be formed which are highly uniform both in thickness and density, these being properties which are specially desirable for optical, antistatic or conductive films serving to modify the optical and/or dielectric properties of bodies or articles to which the said coatings are applied.

Vitreous or partially vitreous bodies or articles of any shape can be coated by means of the method to give them a predetermined tint and particularly, special light reflection characteristics or to give them desired antistatic or conductive properties. It is very advantageous for forming coatings on entirely vitreous transparent bodies and articles, for example windscreens or glazing sheets, because the method enables oxide coatings to be formed which give the article or body various tints as viewed both by transmitted and by reflected light. The method has not only been found suitable for forming a oxide coating directly on a glass or on a surface of partially vitreous material, but also for forming such an oxide coating on an already formed coating film which is adherent to the vitreous substrate, more particularly on an existing metallic oxide coating film such as, for example, a film of titanium oxide or copper oxide.

The oxide coating thickness selected in each given case will depend on the function that the coating is required to perform and may vary, for example, in a range of from some hundred to some thousands of Angstroms. A coating of a given thickness may, if necessary or desirable, be formed from two or more successive layers. The thickness of a coating is best measured by intraferometry, although it is also possible to dissolve the coating, analytically determine the weight of the coating per unit of area, and calculate the thickness, taking into account the known density of the oxide and its degree of compaction as a thin film.

The method may be performed particularly economically in the formation of a coating film on flat glass, by spraying the solution onto a continuous ribbon of glass in course of its production, for example at a coating station located in the drawing chamber of a glass drawing machine or in an annealing gallery. The solution is preferably applied where the glass is at temperatures within the range from 300 to 700°C, preferably between 450 to 650°C, as indicated above. It is advantageous to direct the spray of coating solution perpendicularly onto the glass ribbon, and to reciprocate the device transversely to the direction of advance of the ribbon past the coating station. The method may advantageously also be performed by spraying the solution onto patterned glass during its production in the form of a continuous ribbon. Such a glass moves at a relatively higher speed than flat glass, but this presents no difficulty since the prepared solution may be sufficiently concentrated in order to produce the coating within the time limits imposed by the method of forming the glass.

When a mixture of two or more salts is used, the proportions of the different salts can be adjusted to control the properties of the coating, for example to control the tint of the coating by transmitted and/or by reflected light, or to control its electrical resistance.

It is often desirable to use metallic acetates, halides or nitrates in the perfectly crystalline form. For example, one or more hydrated acetates can be used, such as bivalent cobalt acetate which crystallises with four molecules of water, or anhydrous acetates such as zinc acetate, unless precipitation will involve wastage of coating material.

To obtain films of selected tints as viewed by transmitted and reflected light, it is possible to use mixtures of a plurality of acetates, halides or nitrates dissolved in one or more aprotic solvents having a dielectric constant greater than 15 and a dipole moment greater

than 3D. For example use can be made of mixtures of salts of cobalt, iron and chromium for obtaining coatings which have a bronze tint when viewed by transmitted light and which moreover have good resistance to external conditions even in the presence of an acid.

An advantageous application of the method is the coating of an athermanous glass with a highly reflecting coating without substantially increasing the energy absorption.

The light and energy transmission of a coating of given thickness may be increased without substantially modifying the light or energy reflection, by using suitably selected metallic compounds such as, for example, one or more acetates, nitrates or halides of one or more metals of the group: aluminium, zinc, thorium, cerium, tin and magnesium.

Generally, the presence of water in a relatively high quantity in the film-forming solution is acceptable, but preferably it will not exceed 10% by volume. If the amount of water is excessive, the resulting coating may have very small dark stains which are often referred to as "pitting". It should, however, be noted that the extent to which such defects are visually perceptible if at all, in practice depends partly on a number of other factors and, in particular, the composition and the geometry of the coated surface and the thickness of the coating. The said defects are less perceptible on patterned glass of which the motif is highly compact, on reinforced glass (glass in which wire netting has been incorporated), on profiled glass, for example in the form of a U, and on certain vitrocrystalline materials, than on flat glass having plane surfaces.

Even when the coating is applied to flat glass, such defects tend to be less apparent the greater is the thickness of the coating. On the other hand the greater the thickness of the coating, the more the light transmission of the coating is reduced and in cases where this factor is important the optimum thickness of the coating represents a compromise between the absence of defects and the degree of light tranmission.

For example, a cobalt oxide coating applied to a plane glass surface and having an optical thickness of 500A has a light transmission of 47% and unless the most favourable conditions as herein described are observed in order to produce a defect-free coating, such defects are likely to occur and to be perceptible to the naked eye. If the same solution is applied to form an oxide coating having an optical thickness of 900 Å, the imperfections are difficult to see if not totally invisible, but the light transmission is only 26%.

The hardness of the coatings produced according to the invention using the preferred compositions is generally high. Most of the glazings thus coated may be used as single glazings with the coated surface exposed to ambient conditions, because such coatings are sufficiently resistant to mechanical damage under conditions of normal use. If required however, a protective coating, such as a coating of SnO_2, ZrO_2 or TiO_2, may be superposed, for example, on a coloured coating.

To test the hardness and adherence of coatings produced by means of a method according to the invention, it is possible to use a reciprocating friction element having a surface area of 1 cm^2 and formed by rubber incorporating corundum particles of a diameter of 75—125 microns. The friction element is set in a weighted tube (weight of assembly 100 g) which slides vertically in a support. Constant contact is thus ensured between the friction element and the sample. The friction element assembly is reciprocated by a crank system. The amplitude of the movement is 3 cm and its frequency is one forward and one return stroke per second. After some time the resulting wear pattern consists of scratches very close together with undestroyed coating left between them.

In various tests carried out on glasses coated with oxide coatings such as ZrO_2, SnO_2, SnO_2 and Sb_2O_3, TiO_2, Co_3O_4, Cr_2O_3, Y_2O_3, ThO_2, CeO_2, SiO_2 or a mixture of these oxides, it was found that after 5 minutes 5% of the surface subjected to friction was scratched. At least one hour was required for 95% of the surface to be scratched.

According to certain embodiments of the method, a layer containing tin oxide is formed on a substrate. Such a coating is particularly advantageous because tin oxide gives the coating very considerable hardness.

It is possible, for example, to deposit on a glass substrate, coatings consisting essentially of iron oxide containing a small quantity of tin oxide, i.e. for example 90% Fe_2O_3 and 10% SnO_2, which are coloured and can be used for a single glazing, this not being the case with a coloured coating consisting solely of iron oxide. A coating of this kind is readily produced by spraying on glass a solution of ferric chloride to which there has been added acetylacetone and anhydrous $SnCl_2$ in dimethylformamide.

The presence of tin oxide in a coating which also contains one or more coloured oxides makes it possible to control and dilute the tint as viewed by transmitted and by reflected light.

The presence of tin oxide is also very advantageous when making coatings having anti-static or electrically conductive properties.

To form such coatings, solutions are used which preferably contain one or more tin chlorides which may or may not be anhydrous, i.e. $SnCl_2$, $SnCl_2 . 2H_2O$, $SnCl_4 . 5H_2O$ or $SnCl_4$.

To form coatings having a required electrical resistance, the thickness and composition

thereof are controlled. For example, to produce an antistatic coating on a substrate of vitreous mtaerial, it will be preferable to use a coating containing tin oxide with a thickness between 200 and 800Å.

To obtain a resistance equivalent to an antistatic or a conductive coating it is possible to use coatings which contain small quantities of antimony in addition to tin oxide. To obtain a conductive coating it is preferable to use a salt solution containing a stannous salt as the main ingredient for forming the coating.

The invention will be more readily understood and its advantages will be more apparent from the following non-limiting examples wherein Example 8 has reference to the accompanying drawing which shows the result obtained with one specific embodiment of the invention. The drawing is a graph comprising two curves. Curve 1 denotes the light transmission of a film of oxides comprising SnO_2 and Sb_2O_3 in varying proportions while curve 2 represents the electrical resistance of said film against the amount of antimony salt present in the film-forming solution.

Example 1.

A film-forming solution was prepared by dissolving 199 g of bivalent cobalt acetate crystallised with 4 molecules of water and 73 g of anhydrous zinc acetate per litre of solvent. The solvent selected was dimethylformamide.

The solute prepared in this way, expressed in terms of the corresponding oxides, contained 65% by weight of CoO and 35% by weight of ZnO.

This solution, the temperature of which is held at 70°C, was then sprayed on a ribbon of glass in course of its continuous production by a drawing process in which the glass ribbon ascends through an annealing gallery, the spraying being carried out at a place where the glass ribbon had a temperature of 590°C.

An internal mix spray gun was used which was fed with the solution and compressed air both at a pressure of 3.5 kg/cm² above atmospheric pressure.

The distance between the mouth of the gun and the sheet of glass was 25 cm. The gun was reciprocated continuously transversely to the direction of advance of the ribbon, the speed of advance being 1.5 m per minute. The reciprocating movement of the gun had a forward and return stroke period of 6 seconds (glass ribbon width: 3 m).

The output of the gun was 12.7 litres of solution per hour, equivalent to a solution flow of 47 cm³ per m² of glass ribbon. The solution was sprayed to give a film of a thickness of 650 Å.

The film had a uniform thickness and was free from pitting.

After cooling of the glass, an optical film was obtained which had a green tint in transmitted light and was highly reflective. The coated glass product had the following properties, defined and calculated according to M. Leger in "Silicates Industriels", February 1964, pp 47—56:

Global luminous transmission:	70.5%
Luminous reflection from coated side:	14.8%
Luminous reflection from uncoated side:	16.0%
Global solar energy transmission:	69.7%

With coated side facing global solar energy source:

Global solar energy reflection from coated side:	13.7%
Global solar energy absorption of product (glass + coating):	16.6%

With uncoated side facing global solar energy source:

Global solar energy reflection from uncoated side:	13.9%
Global solar energy absorption of product:	16.4%

A similar result was obtained by replacing the dimethylformamide by another solvent such as dimethylacetamide, tetramethyl urea, dimethylsuphoxide, acetonitrile, nitrobenzene, ethylene carbonate, tetramethylsulphone or hexamethylphosphoramide.

Example 2.

79 g of chromium nitrate ($Cr(NO_3)_3.9H_2O$) were dissolved in 0.8 litre of dimethylformamide. 58.5 cc of acetylacetone were then added. The mixture was heated for 15 to 20 minutes at a temperature of 50°C. Heating was then stopped and during the cooling of the solution 52.8 g of ferric chloride $FeCl_3 . 6H_2O$ were dissolved and 58.5 cc of acetylacetone were added.

169 g of bivalent cobalt acetate ($Co(CH_3COO)_2.4H_2O$) and 23 cc of acetylacetone plus 34.9 cc of H_2O_2 were then added to the resulting solution. The hydrogen peroxide served to convert the bivalent cobalt to trivalent cobalt. The solution was agitated with cooling for about 15 minutes. Dimethyl formamide was added to make up 1 litre of solution. The resulting solution had a total solute concentration of 85.1 g/litre of solution, the solute (expressed as oxides) having the following composition in percentage by weight:

64.1% Co_2O_3
18.4% Fe_2O_3
17.5% Cr_2O_3

This solution was then sprayed on to a glass ribbon 4 mm thick made in the same way as in Example 1. The temperature of the glass during the spraying operation was 600°C.

The equipment used for spraying was the same as in Example 1.

The gun output was 13.8 litres of solution per hour.

The coating deposited had a uniform thickness of 800 Å and had a bronze tint when viewed in transmitted light.

The oxides composition in the coating was, by weight,

12% Fe_2O_3
18% Cr_2O_3
17% Co_3O_4

The light transmission was 47.1%

The energy transmission was 51.3%

When the thickness of the coating was increased to 1200 Å, a more yellowish tint was obtained when viewed in transmitted light.

In that case the light transmission was 36.7% and the energy transmission was 42.6%.

The coating obtained had sufficient hardness for use as single glazing and also had excellent resistance to external conditions, including acids.

The same operation was repeated on printed glass while it was at a temperature of 640° during production. A coating of oxides of a thickness of 540 Å was deposited on this glass using identical spray equipment to that described above. The solution delivery was 16.1 litres per hour and the speed of movement of the glass was 3.15 metres per minute (ribbon width 2 metres).

Example 3.

113.5 g of zirconium chloride ($ZrCl_4$) were dissolved in 0.8 litre of dimethylformamide. The solution was then made up to 1 litre to have a concentration equivalent to 60 g of ZrO_2 per litre of solution. This solution has a yellowish tint and is cloudy.

This solution was then sprayed on to a sheet of glass at a temperature of 600°C. The resulting coating was of a grey tint and had a number of small bright spots.

The same test was repeated but with the addition of acetylacetone to the starting solution, the proportion of acetylacetone used being 4 moles to 1 mole of $ZrCl_4$. The amount of acetylacetone added was 195 cc. After heating to 50°C for about 15 minutes the solution became perfectly clear.

When this solution was sprayed on to the sheet of glass the resulting film was perfectly uniform and grey when viewed in transmitted and reflected light.

The characteristics of the resulting product were as follows:

Light transmission 73.8%
Energy transmission 74%
Light reflection on coating side 22.8%
Energy reflection on coating side 18.2%

The resulting coating was very hard.

Example 4.

A number of film-forming solutions were prepared by dissolving the metallic salt corresponding to the desired oxide in an appropriate solvent. The solutions, which are shown in the Table below, were sprayed on to a sheet of glass 4 mm thick heated to a temperature of 600°C. The characteristics of the resulting products are shown in the Table.

Starting Salt	Solvent	Composition of Film	Thickness of film	Properties of the film and of the product obtained
$Mg(CH_3COO)_2$	DMSO	MgO	400 Å	Light transmission 79.3% Energy transmission 77.4%
$BiCl_3$ (+Acac)	DMF	Bi_2O_3 50%	700 Å	Yellow when viewed in transmitted light after assembly in double glazing: Light transmission 57.6% Energy transmission 59.5% (The film was disposed on the inner surface of the outer glass).
VCl_3 (+Acac)		V_2O_5 50%		
$Cd(CH_3COO)_2.2H_2O$	DMF	CdO	400 Å	Light transmission 79.3% Energy transmission 77.4%
WCl_6	acetonitrile	WO_3 80%	500 Å	Grey tint in transmitted and reflected light Light transmission 67.7% Energy transmission 70%
$MoCl_5$		Mo_2O_3 20%		
$Pb(CH_3COO)_2$ (+5cc litre HAc)	DMF	PbO 60%	500 Å	Grey-brownish tint in transmitted light Light transmission 67.7% Energy transmission 71.3%
$Mn(NO_3)_2.6H_2O$		MnO_2 40%		
$AuCl_3$	DMF	Au 14.95%	650 Å	The effect of the presence of Rh_2O_3 is to limit the dimensions of the particles of Au. Film of blue tint in transmitted light. After assembly as double glazing the following values were obtained: Light transmission 57.1%, Light reflection 17.2%, Energy absorption 28.9% Energy transmission 56.2% Energy reflection 14.9%
$ThCl_4$ (+Acac)		ThO_2 70%		
$TiCl_4$ (+Acac)		TiO_2 15%		
$RhCl_3$		Rh_2O_3 0.05%		

(Continued)

Starting Salt	Solvent	Composition of Film	Thickness of film	Properties of the film and of the product obtained
FeF_3 (+Acac)	dimethyl-acetamide	Fe_2O_3 75%	550 Å	Yellow-amber tint in transmitted light, yellow in reflected light
$CrBr_3$		Cr_2O_3 25%		Light transmission 52.5% Energy transmission 54.6%
$Zr(NO_3)_4.5H_2O$ (+Acac)	DMF	ZrO_2 60%	600 Å	Brown tint in transmitted light Light transmission 56.7%,
$Ni(NO_3)_2.6H_2O$ (+Acac)		NiO 10%		Light reflection 29.5%, Energy absorption 14.3%,
$Cu(CH_3COO).H_2O$		CuO 30%		Energy transmission 63.7%, Energy reflection 22%
$CeCl_3$ (+Acac)	DMF	Ce_2O_3 85%	400 Å	Grey tint in transmitted and reflected light
$Al(NO_3)_3.9H_2O$ (+Acac)		Al_2O_3 15%		Light transmission 71.2% Energy transmission 72.5%
$SnCl_4.5H_2O$	DMF	SnO_2 90%	700 Å	Pink tint in transmitted light Light transmission 71.8%
$AsCl_3$		As_2O_3 10%		Energy transmission 69.1%

DMSO = dimethylsulphoxide DMF = dimethylformamide Acac = acetylacetone

HAc = acetic acid

Example 5.

Tin oxide coatings were prepared by spraying solutions of tin chloride in dimethylformamide.

3 solutions were prepared by dissolving each of the following in dimethylformamide: $SnCl_2$; $SnCl_2 . 2H_2O$; $SnCl_4 . 5H_2O$.

A fourth solution was prepared by initially dissolving $SnCl_4$ in acetylacetone to give a very viscous red liquid which was then dissolved in dimethylformamide.

These four solutions had an identical tin content and were sprayed onto a sheet of glass at a temperature of 580°. The coatings obtained from the four solutions were identical optically. Their tint was green in reflected light in all four cages.

Example 6.

A film-forming solution was prepared by dissolving 400 g of stannous chloride ($SnCl_2 . H_2O$) and a small quantity of antimony chloride, i.e. 7.5 g of $SbCl_3$, in one litre of dimethylformamide.

Molar ratio in soln ≠ molar ratio in coating

This solution was sprayed at a flow rate of 15.8 litres per hour onto the smooth surface of a printed glass ribbon moving at a speed of 3.5 metres per minute, just upstream of the annealing gallery, at a place where the temperature of the glass was of the order of 680°C. The total width of the ribbon was 1.57 m. The gun was reciprocated over a distance of 1.27 m. The number of sweep cycles was 25 per minute.

A coating having a uniform purple tint was obtained over a width of 1.10 m. The thickness of the coating was 2700 Å. The electrical resistance of the coating was 60 Ω/□. A piece of glass 30 × 30 cm was cut from this ribbon and subjected to thermal hardening. Silver varnish electrodes were then attached. With the application of a voltage of 220 V, the temperature a few millimetres above the glass was 92°C. If a coating of less thickness is deposited, i.e. 200 to 800 Å, the same starting solution yields an antistatic coating which is no longer electrically conductive.

It was also possible to obtain antistatic coatings by spraying onto the glass a film-forming solution containing from 70 to 90% by weight of $SnCl_4$ and 30 to 10% by weight of $SnCl_2$.

Example 7.

Stannic chloride ($SnCl_4$) was dissolved in acetylacetone and then the resulting liquid was dissolved in dimethylformamide and ferric chloride ($FeCl_3 . 6H_2O$) was added thereto.

Different solutions containing different proportions of stannic salt and ferric salt were sprayed onto a glass heated to 550°C.

The concentration (as oxides) was always 60 g per litre and the thickness of the film was of the order of 500 Å.

The following table gives the compositions of the solutions used and of the films obtained. It will be seen that the conversion of the tin and iron salts by pyrolysis was not 100% efficient.

Composition of solute (as oxides) %	SnO_2	0	10	20	30	40	100
	Fe_2O_3	100	90	80	70	60	0
Composition of the film (%)	SnO_2	0	25	41	64	79	100
	Fe_2O_3	100	75	59	36	21	0
Light transmission (%)		50.3	55.2	60.1	65.6	71.1	76.8
Tint		Pronounced yellow amber	Amber grey	Amber	Yellowish Grey	Grey	Pale grey

Example 8.

75.5 g of anhydrous $SnCl_2$ and 15 g of $SbCl_3$ were dissolved in 1 litre of dimethylformamide. The solution was sprayed onto a sheet of glass to form a coating with a thickness of the order of 2000 Å.

The coating had a very intense blue tint when viewed in transmitted light.

Light transmission of the order of 21%.

Light reflection 5%.

By adjusting the concentration of the $SbCl_3$ it is possible to vary the intensity of the blue tint and also the resistance of the coating. This is illustrated by the accompanying graph in which the curve 1 represents the light transmission of the film against the quantity of $SbCl_3$ present in the film-forming solution and curve 2 represents the resistance of the film against the quantity of $SbCl_3$ present in the solution.

The curves 1 and 2 were plotted from the following data: the light transmission of the film of a thickness of 700 Å (as a percentage) was plotted against the left-hand ordinate and the electrical resistance in Ω/□ was plotted against a logarithmic scale on the right-hand

ordinate. The abscissa represents the number of grams of $SbCl_3$ added to a litre of solution containing 75.5 g of anhydrous $SnCl_2$.

Example 9.

127 g of indium chloride ($InCl_3 . 4H_2O$) were dissolved in 1 litre of dimethylformamide. 1.58 g of $SnCl_2$ were added thereto (to give 2% of metallic Sn based on metallic In content).

The solution was sprayed onto a glass heated to 500°C so as to give a coating of the order of 1200 Å thickness.

A coating of this kind was of a blue tint in reflected light and slightly yellowish in transmitted light.

Light transmission 87.2%
Energy transmission 79.5%
Electrical resistance 70 Ω/□

A coating of this kind may be used as a glazing for heating purposes. It was found that the addition of a small quantity of acetylacetone to the film-forming solution (i.e. 1/3 mole of acetylacetone to 1 mole of $InCl_3 . 4H_2O$) improved the optical quality of the film and that it was possible to obtain films with an electrical resistance of 25 Ω/□ and even less.

Example 10.

A spraying solution was prepared by diluting silicon chloride ($SiCl_4$), to which acetylacetone had been added, in dimethylformamide.

The solution was sprayed on to a sheet of glass heated to 500°C to form a very thin film of SiO_2 of the order of 150 Å thick.

An indium oxide coating identical to that indicated in Example 9 was then deposited on the glass coated in this way.

The optical and electrical properties of the coating were similar to those obtained in Example 9, the quality and uniformity of the coating being particularly high.

Solvents can be classified as "protic" (acid) or "aprotic" (basic) solvents. Protic solvents are hydrogen-donors. Solvents having a dielectric constant higher than 15, and which although they may contain hydrogen atoms are unable to form strong hydrogen bonds, may also be called "dipolar aprotic solvents" (c.f. PARKER, A. J. "The effects of solvation on the properties of anions in dipolar aprotic solvents" Quarterly Reviews, *16*, p. 163 (1962)).

Reference has been directed under Section 9(1) of the Patents Act, 1949, to United Kingdom Patents Nos. 1293061 and 1292479.

WHAT WE CLAIM IS:—

1. A method of forming a coating on a substrate, the coating comprising an oxide or oxides of one or more metals and/or of silicon, wherein a solution comprising at least one metal compound and/or a silicon compound is applied to the substrate and the said compound or compounds is/are converted *in situ* by the action of heat so as to form a said coating, the said solution which is applied to the substrate being a solution of one or more metallic salts and/or a silicon salt selected from the group of the acetates, halides and nitrates in an aprotic solvent having a dielectric constant greater than 15 and a dipole moment greater than 3D.

2. A method according to claim 1, wherein the substrate is preheated to a temperature high enough to provide the heat required to effect the said conversion of the applied compound or compounds.

3. A method according to claim 2, wherein the substrate is preheated until the surface to be coated reaches a temperature of between 300 and 700°C.

4. A method according to any of the preceding claims, wherein the solution is applied in the form of droplets.

5. A method according to any of the preceding claims, wherein dimethylformamide is used as the solvent.

6. A method according to any of claims 1 to 4, wherein the solvent used is selected from the group dimethylacetamide, tetramethyl urea, dimethyl sulphoxide, acetonitrile, nitrobenzene, ethylene carbonate, tetramethylene sulphone, and hexamethylphosphoramide.

7. A method according to any of the preceding claims, wherein the solution applied to the substrate comprises one or more acetates, halides or nitrates of an element or a plurality of elements selected from the group: Mg, Zr, V, Cr, W, Mn, Fe, Co, Ni, Cu, Zn, Cd, In, Sn, Pb, Bi, Th, Si.

8. A method according to claim 7, wherein the solution also comprises one or more acetates, halides or nitrates of a metal or of a plurality of metals selected from the group: Au, Ti, Ce, Mo, Sb, Al, As, Rh.

9. A method according to any of the preceding claims, wherein the solution also contains acetylacetone.

10. A method according to claim 9, wherein the solution contains acetylacetone in a proportion such that the number of moles of acetylacetone used is *n* times the number of moles of salt used (where *n* represents the valency or the aggregate of the valencies of the cations(s)).

11. A method according to any of the preceding claims, wherein the said solution is applied to a substrate which is vitreous or partly vitreous.

12. A method according to claim 11, wherein the said solution is applied so as to form an oxide coating which is transparent to light.

13. A method according to any of the preceding claims, wherein the substrate is flat glass which is in the course of being manufactured as a continous ribbon.

14. A method according to claim 13,

wherein the said solution is applied to the glass ribbon in a zone where the temperature of said ribbon is between 450 and 650°C.

15. A method according to any of the preceding claims, wherein the solution used is formed wholly or in part from one or more tin chlorides (hydrated or anhydrous).

16. A method according to claim 15, wherein the oxide coating formed has antistatic properties.

17. A method according to claim 16, wherein the coating has a thickness of 200—800 Å.

18. A method according to claim 1 and substantially according to any of the Examples herein.

19. A vitreous or partly vitreous substrate bearing an oxide coating formed by means of a method according to any of the preceding claims.

20. A non-vitreous substrate bearing an oxide coating formed by means of a method according to any of claims 1—10 and 15—17.

HYDE, HEIDE & O'DONNELL,
Chartered Patent Agents,
47 Victoria Street, London, SW1H 0ES.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1455148 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*